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Flame Retardant Nano-Composites containing Nano-Fillers

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Introduction

There is a worldwide trend of using high Non-flammability polymer materials in construction, cars, aircrafts, and ships, even though they are in electrical devices. A normal polymer material is basically inflammable; to overcome the material's limit, a halogen element is normally used. Including a halogen material has been shown to give a high degree of flammability, but in their consuming state, they produced toxicant intermediates. This result is more harmful to refugees and the environment, whether they attain high flammability or not. For this reason, many governments, including the United States of America (US) and the European Union (EU), have established restrictions and regulations regarding flame-retardants and using halogenate material and diphenyl oxide. In addition, the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) recommend a limit on the exposure amount for the risk assessment of toxic components [1, 2]. Following that, a new flame retardant material should be developed to satisfy new regulations.

Many flame retardant systems, including organic intumescent agents, metal hydroxide and hydrocarbonates, phosphorus-based (red phosphorus, inorganic phosphorus, and organic phosphorus), nitrogen-based, silicone, silica and nanometric materials (nanoclays, carbon nanotubes, graphene), were designed and investigated [3].

Metal hydroxide systems have shown good performance, but they need a high amount of loading; furthermore, purity and morphology can easily affect performance. However, this material has been limited by the high cost of production. For example, magnesium hydroxide decomposes to magnesium oxide with water endothermically (1,450 J/g) [4].

To overcome this drawback, nanometric materials are very affordable and convenient to combine with a composite master batch. Therefore, in this chapter, we focused on nanometric flame-retardant systems and the synergetic effect with intumescent agents.

Nano Clays

Nanoclays are classified depending on their element composition, electrical charge grade, and dimension. When depending on elements, they are divided into many categories with the following main big groups: montmorillonite, smectite, kaolinite, chlorite, and illite. Electrical divisions consist of two categories: cationic and anionic. Following this property, the surface treatment process and surfactant material should be changed. Finally, clay shapes are categorized as nanolayer, nanoparticle, nanotube, and whisker. Additionally, clay can be divided based on their creation pathway, of which there are three types: natural, incidental, and synthetic nanoparticles [5].

Many kinds of clays exist. However, when making a flame retardant nanocomposite, one typically uses layered silicates that are synthesized or originate from nature. Among the clays, the cationic layered silicate type of clay is domestically used for manufacturing composites. This clay's structure is specified as a layered crystal structure and consists of a tetrahedral structure, a silicon atom surrounded by four oxygen atoms and an octahedral sheet with metals (aluminum, iron, magnesium, and lithium) by eight oxygen atoms, like shown in Figure 1.1. The clay layer thickness is approximately 1 nm, and the lateral dimension range is dependent on the class of clay and synthesis process, from the smaller 20 nm to the larger micron scale [6].



Structure of 2:1 phyllosilicates [6] Reproduced with permission. Copyright 2003, Elsevier Ltd.

Montmorillonite (MMT) and saponite are the most commercially and wildly used materials. A common formulation of MMT is (Na, Ca)0.33(Al, Mg)₂(Si4O10)(OH)₂·nH₂O. MMT has been measured and has a high aspect ratio in a well-dispersed nanocomposite with a high surface area of approximately 750 m²g⁻¹ [7, 8]. For these reasons, MMT has shown good flame-retardancy when added to a polymer composited material as a nanofiller.

Halloysite is a hollow tube type of clay, is rolled up to form a bilayer, and has a chemistry division considered to be kaolinite, has recently attracted attention [9]. Halloysite nanotubes (HNTs) originate from nature as an aluminosilicate. Some clay exists in a layered state, but predominantly many clays exist as a hollow shape structure. In general, clay has an electrical interaction between clay layers, but the HNTs have no interaction between clay layers because they are rolled up and the electrical interaction cancels itself in intra-clay; however, some interactions exist via hydrogen bonds and van der Waals forces. Therefore, HNTs' dispersion is easier than layered silicate dispersion in a polymer nanocomposite [10].

Other kinds of clay can also be used as a nanometric material in a polymer composite, but this chapter concentrates on montmorillonite and halloysite nanotubes.

Surface modification of clay

When nanoclay is used in a composite as a flame retardant nanometric additive, dispersion is a very important factor to accomplish the flame retardant property. Layered silicates inevitably have electrical interactions; their chemical structure creates an imbalance in charge, so a treated silicate layer appears as a stacked clay colony in a polymer matrix. This stacked clay cluster reduces the specific surface area and consequently impoverishes the flame retardant property of the polymer composite [11].

In Figure 1.2, the clay dispersion state can be classified in three states: phase separated, intercalated, and exfoliated. Exfoliated clay is the ideal state to use as a polymer nanocomposite numerical additive. Their specific surface area increases following the silicate layer intercalation and exfoliation. For the interaction between the silicate and polymer, the specific surface area is an important factor influencing the polymer composite's mechanical and flammability properties.



FIGURE 1.2

Scheme of different types of composites arising from the interaction of layered silicates and polymers: (a) a phase separated micro-composite, (b) an intercalated nanocomposite and (c) an exfoliated nanocomposite. [11] Reproduced with permission. Copyright 2000, Elsevier Ltd.

Pristine layered cationic clay interlayers contain charged Na+ or K+ ions [12]. In the clay organomodification process, an organic surfactant is commonly used. Hence, the interlayer ions' replacement surfactant incises the clay d-spacing, and the d-spacing showed differences, depending on the replacement level and surfactant tail length [13]. Such an organic surfactant modified layered clay has a positive effect on the dispersity in a composite. However, organic surfactants have a single carbon chain, and a single conjugation linkage inevitability has a low thermal stability. Therefore, when a nanocomposite is exposed to surrounding heat and consumption, the surfactant consequentially has a bad influence on the composite's thermal stability and flammability.

In this chapter, which is focused on flame retardancy, the author considers that this drawback can be overcome while sustaining the clay d-spacing. A thermally stable material for use as a clay surface modification ingredient can make a thermally stable polymer nanocomposite, while at the same time maintaining clay dispersion.



(a) Schematic of clay intercalated with POSS. (b) X-ray powder diffraction patterns of intercalated clay by POSS, pure clay, and pure POSS. (c) TEM micrographs of POSS-treated nanocomposite. [15, 16] reproduced with permission. Copyright 2004, 2011, Elsevier Ltd.

Polyhedral oligomeric silsesquioxane (POSS) molecules are typically stable to over 400°C, which is higher than the thermal degradation temperatures of most organic molecules [14]. The use of amine-functionalized POSS or amine-POSS enabled an ionic exchange reaction and the surfactant's incorporation into the clay interlayer spacing (Figure 1.3) [15, 16]. The resulting nanocomposites exhibited an enhanced thermal stability up to 300°C because of the presence of the silicate clay. The intercalation of amine-POSS salts into clay galleries was evidenced by an increase in the interlayer spacing from 1.26 to 1.61 nm. The polystyrene/clay nanocomposites, which were produced by incorporating the amine-POSS/clay hybrid, exhibited an exfoliation of the clay platelets (TEM image in Figure 1.3c) and an enhanced thermal stability compared with pristine polystyrene [17].

Another way that is also considerable is using an agent containing a phosphate element. The phosphate functions as an intumescent agent and as a radical scavenger. A phosphate containing clay surface modifying material was designed, 2-(2-(5,5-dimethyl-1,3,2-dioxaphosphinyl-2-ylamino)ethy-amino)-N,N,N-triethyl-2-oxoethanaminium chloride, and contains a phosphorus–nitrogen structure (compound C). Compound C can successfully substitute for the Na+ ions between silicate interlayers, as shown in Figure 1.4, and improve both the dispersion in the polymer matrix and the flame retardancy of MMT [18].



(a) Schematic of the substitution of Na+ by 2-(2-(5,5-dimethyl-1,3,2-dioxaphosphinyl-2-ylamino)ethy-amino)-N,N,N-triethyl-2-oxoethanaminium chloride, containing a phosphorus–nitrogen structure. [18] Reproduced with permission. Copyright 2010, Elsevier Ltd.

Many methods exist to modify the clay surface. Clearly, the clay surface electrical property is an important factor on the clay dispersity in the polymer matrix, though the nanoclay dispersity in the polymer composite is a correlated nanocomposite preparation process. This point will be discussed in the nanocomposite preparation chapter.

Other Nanomaterial

For flammability, many kinds of nanometric material can be introduced, and among them, carbon nanotubes (CNT) and graphene are notable. Carbon nanotubes are well known and wildly used in polymer composites. There are two types of CNT, the single-wall type (SWNT) and multiwall carbon nanotubes (MWNT) [19]. However, just for flammability, using SWNT has the drawback of a cost problem; therefore, MWNT are wildly used and researched. Compared with the nanoclay, MWNT have shown more respectable flammability properties and a thermostability about efficiency. While MMT reached a flammability performance at a 0.135 mass fraction, MWNT need a 0.0003 mass fraction (in N2 atmosphere) to reach a similar state [20].

Above, the 'surface modification of clay' chapter mentioned the importance of clay surface modification. Compared with clay, the CNT (MWNT, SWNT) do not require surface modification because they consist of sp2-bonded carbon atoms rolled into a seamless cylinder and its surface electrical charge is close to that of a general polymer resin [19]. Additionally, the nature of the dispersion problem for CNT is rather different from those of other conventional fillers, such as spherical particles and carbon fibers, because CNTs are characterized by a small diameter on the nanometer scale with a high aspect ratio (>1,000) and thus have an extremely large surface area. In addition, the commercialized CNTs are supplied in the form of heavily entangled bundles, resulting in inherent difficulties in their dispersion [21]. To resolve the CNT bundle issue, mechanical and chemical treatments are required. The mechanical treatment uses the signification method in a solvent matrix state, while the chemical treatment uses a surface modification method [21, 22].



Schematic illustration for the synthesis of MWNT-PDSPB (poly-diaminodiphenyl methane spirocyclicpentaerythritol bisphosphonate). [24] Reproduced with permission. Copyright 2008, John Wiley & Sons, Inc.

The MWNT surface modification has the benefit of solving the CNT bundle in a solution environment, but a future chapter explains about the low thermal stability of the surface modification molecule and its effect on the polymer composite's flammability. To overcome the drawback of CNT surface modification using a molecule containing phosphate like with clay modification (Figure 1.5), the CNT surface electrical property should be different than that of the clay surface. Therefore, to attach a molecule to a CNT, one should create functional groups on the surface. For the CNT treatment, covalent approaches exist such as halogenation at high temperature, hydrogenation, cycloaddition, radical addition, electrophilic addition, addition of Inorganic compounds, ozonolysis, and many other possible methods [23].

MWNTs were treated with nitric acid and thionyl chloride and then reacted with polydiaminodiphenyl methane spirocyclicpentaerythritol bisphosphonate (PDSPB), as shown in Figure 1.5, finally obtaining MWNT-PDSPB. MWNT-PDSPB has good dispersion in organic solvents, and this property is an important factor in making polymer nanocomposites when using the solvent method. The dispersity of a polymer nanocomposite affects the rheology, storage modulus (G'), and loss modulus (G'') of ABS/MWNT and ABS/MWNT-PDSPB nanocomposites are increased at 200 °C. For flammability, the ABS/MWNT-PDSPB nanocomposites show a peak heat release rate (PHRR) that is better than that of the ABS/MWNT composite. In brief, the grafting of the intumescent flame retardant PDSPB can improve both the dispersion of nanotubes in the polymer matrix and the flame retardancy of the nanocomposites [24]. Graphene is also a well-known material and has been widely studied; like CNT, graphene also consists of monolayer of an sp2-hybridized carbon honeycomb two dimensional lattice and shows superior mechanical and electrical properties. In particular, many papers have been published about graphene polymer nanocomposites, and this is the reason why we studied this material's advantageous properties. Graphene has sp2-covelent bonding, which is a feature allowing interaction between layers, making polymer nanocomposite surfaces resistant to dispersion, and additionally providing flame retardancy and thermal stability, in polymer resin [25].

Basically one- and two-dimensional nanometric filler's flame retardant property is due to the formation of their nano- and microscale structure, and they interrupt thermally degraded intermediate materials from moving and meeting oxygen in the atmosphere. Graphene and clay have layered two-dimensional shapes. The clay atom formation is made by silicate, metal, and salt atoms, but graphene consists of only sp2 conjugated carbon. Therefore, the specific surface area of graphene is larger than that of a silicatenanoclay, and it shows a high efficiency of flammability when used as a nanometric additive in a polymer nanocomposite compared with a silicate clay nanocomposite [26].

Two-dimensional nanometric materials used in polymer composites show good flammability, and an additional organic flame retardant can be added to the polymer nanocomposite to provide a synergistically good flammability. This phenomenon will be explained in the next chapter in more detail. When POSS and graphene are added with melamine polyphosphate as nanometric additives in a polymer nanocomposite by melt blending, the synergetic flammability has a different appearance. Zero-dimensional POSS does not enhance flammability properties, but then again, graphene added to a composite shows increasing flammability because of the nano-reinforcement and barrier effects of its unique structure, which is more suitable to manufacture flame retardant PBS composites [27].

As one- and two-dimensional nanometric materials, CNT and graphene can give flammability to a polymer composite, and they can be used together to show a combination effect. Additionally, an intumescent flame retardant (IFR) system in combination with CNTs and graphene was utilized to fabricate PP nanocomposites with an improved flame retardancy. This result confirms that when composite residue after cone calorimetry is examined, the intumescent char enhanced with carbon nanotubes and graphene nano-sheets was formed for the IFR/CNT/Graphene nanocomposites, which inhibited the transmission of heat and mass when exposed to a flame or heat source; thus, the flame retardant properties of the nanocomposites were improved [28].

Next, we discuss intumescent flame retardant-functionalized carbon nanotubes. Graphene has the same sp2-conjugated carbon chemical structure; therefore, one can synthesize an intumescent flame retardant poly piperazinespirocyclicpentaerythritol bisphosphonate (PPSPB) on graphene oxide's (GO) surface to obtain GO-PPSPB, and this process is similar to Figure 5. GO-PPSPB is mixed with polyethylene vinyl acetate through a melt process, and this composite shows a peak heat release rate (PHRR) 56% less than that obtained with a pure EVA resin; thus, the resultant GO-PPSPB forming a char layer hinders the consuming process. In brief, the grafting of the intumescent flame retardant PPSPB can improve both the dispersion of graphene in the polymer matrix and the flame retardancy of the nanocomposites [29].



Preparation route of poly piperazinespirocyclicpentaerythritol bisphosphonate (PBTP), functionalized graphene oxide (GO) and the graphene flame retardant (GFR). [30] Reproduced with permission. Copyright 2013, Elsevier Ltd.

Any other type of flame-retardant can also be integrated with the novel graphene. In the ahead paragraph, we talk about a phosphorus- and nitrogen-containing flame retardant system, they each have a function and specific property. Now, we talk about a silicone-containing hybrid flame retardant system, and the silicon-specific property under consumption shows thermal and thermo-oxidative stabilities by converting to silicon dioxide, which can improve the composite's flammability by fortifying a char barrier to inhibit flammable intermediate products from leaving the composite inner matrix to the consuming surface. Graphene and silicon both have a good thermal stability, so a hybrid system is likely to show good flame retardancy. 3-Aminopropyltriethoxysilane and benzene phosphorous oxydichloride were used for the synthesis of phenyl-bis-(triethoxysilylpropyl) phosphamide (PBTP). This was reacted with graphene oxide, and finally a graphene flame retardant (GFR) was obtained like the one shown in Figure 1.6. The

graphene flame retardant and monomer make an epoxy resin nanocomposite, and their thermal stability and flammability properties were investigated. Only 1 wt% of GFR was added to show a significant reduction of HRR by 43% [30].

Once it is known that a representative nanometric flame retardant material's basic mechanism is based on a geometric property, through surface treatments, it is possible to get additional flammability by using phosphorus and nitrogen elements.

Intumescent agents

To produce a superior grade of flame retardant polymer nanocomposite, just using novel nanometric additives is insufficient to overcome the lack of efficiency; using an intumescent agent is essential. Investment of novel nanometric additives for flammability is based on their geometrical hindering effect; they have obvious limits, whereas an organic intumescent agent system based on a chemical reaction is expected to exhibit a synergetic effect regarding flammability [31-33].

In the last century, mankind has developed polymer and polymer composite materials. They are widely used and need flammability. At first, intumescent agents containing halogenated materials were used, but as time went on, environmental regulations were established. A halogen-free intumescent system is in demand. Today's intumescent agent consists of a phosphorus element, di functional hydroxyl carbon, a nitrogen source, and a tree compound [34, 35]. These intumescent flame-retardants are highly efficient in olefin polymers, and they consist of ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MA). Ammonium polyphosphate (APP) functions as an acid source to scavenge radicals and as a carbonization agent; pentaerythritol (PER) has a role as a char forming agent, and melamine (MA) is for making nitrogen gas during the thermal degradation process. These intumescent systems have complicated mechanisms, as shown in Figure 1.7, in olefin polymer composites [36].

The flammability of intumescent agents contains notable processes of carbonization and making a char layer. These processes are derived from a chemical reaction, and it takes some time to accelerate the suing zeolite for the carbonizing process. Zeolite consists of aluminosilicate, silicon dioxide, and a variety of cations, such as Na+, K+, Ca2+, and Mg2+, in an unstable electrical state that can affect the chemical reaction during the thermal degradation process. A study on the thermal degradation residue of an intumescent zeolite polymer composite by X-ray photoelectron spectroscopy (XPS) found evidence that the pyridinic function of zeolite may participate in the improvement of the fire proofing properties of the material [37]. Following similar reasons, using metal chelates can confirm the composite's enhancement of flammability and thermal stability [38]. The intumescent agent system mainly consists of three components: an aced source using ammonium phosphate, a carbonization agent using a multifunctional alcohol, and a blowing agent using melamine; the component's flammability is dependent on the ratio recipe [39, 40]. However, these systems have a basic problem regarding the hydrophilic property of pentaerythritol; they have hydroxyl groups in the molecular structure, making for a moisture sensitivity problem, which will decrease flammability and mechanical strength in the olefin polymer composite [41]. To overcome these drawbacks, they synthesized a component that is a novel halogen-free phosphorus-containing caged bicyclic carbonization agent (BCPPO, Figure 1.8-a), which is hydrophobic in nature and shows a high thermal stability because of the symmetrical structure and the incorporation of a benzene group, and was successfully synthesized by a nucleophilic substitution reaction at a low temperature. When used in a polypropylene composite, the material

shows good flammability and dripping resistances, and exhibits a synergetic effect with APP (acid source) and MA (gas source) [42].



FIGURE 1.7

Chemical reactions in olefin polymer composite intumescent formulations. [36] Reproduced with permission. Copyright 2005, John Wiley & Sons, Ltd



(a) Synthesis route of bis(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxo-4-hydroxymethyl) phenyl-phosphonate (BCPPO). (b) Synthesis of bis(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol) chlorophosphate. [42, 43] Reproduced with permission. Copyright 2005, 2007, Elsevier Ltd.

The next paragraph mentions the synthetic phosphor element and pentaerythritol. However, one can synthesize a novel phosphorus-nitrogen containing compound for use as a new intumescent flame retardant that concentrates all of the three elements in itself, like Figure 1.8-b [43].

Both cases of synthesized flame retardants show excellent flame retardancy in a polymer composite [42, 43]. Additionally, it is worth mentioning about the use of silica-containing materials as a synergetic material in a polymer composite. Normal flame retardants have some drawbacks compared with the halogen-element-containing flame retardants [44], for instance, a low flammability efficiency. Therefore, to overcome the drawback, one should develop a new flame-retardant system. It was found that many researchers have shown that synergistic agents can effectively increase the strength and stability of the char layer by Si–O–P–C and Al–O–P–C bonds [45, 46]. Thus, using a general silicon compound, hydroxyl silicone oil, with common flame-retardant compounds (APP and PER) can make a polymer (PP) composite. These composites show an increase in the efficiency of the intumescent char shield, and the chemical catalytic action of the solid acids derived from the reaction of APP and SiO₂ occur on the surface of the burning composite further reduce the HRR of the composite [47].



Possible flame retardant mechanism of the IFR-poly butylene succinate (PBS) composite with fumed silica. [48] Reproduced with permission. Copyright 2010, American Chemical Society.

In addition, fumed silica can also be used as a synergetic additive in a polymer intumescent composite, and it shows similar results regarding flammability and the same chemical reaction in the consumption stage. Figure 1.9 shows the silica particle's role during combustion. They show the chemical and structural role of silicate. Fumed silica was easy to accumulate on the sample surface because of its large surface area, low density, and low superficial free energy in heating. Thus, a flame retardant PBS with fumed silica could form a physically strong charred surface layer during combustion. The more stable intumescent charred layer could not only effectively prevent the melt from dripping but also hinder the propagation of oxygen and heat into the interior substrate [48]. These intumescent flame retardants show a synergetic effect with the silicate material. In this part, we talk about the possibility of a synergetic effect with the silicate material by chemical and structural means on the molecular and micro level. The next section will talk about the synergetic effect between the nanoclay and the intumescent agent system.

Nanocomposite preparation

The polymer nanocomposite preparation methods are classified as three big methods referring to the dispersion technique: the solution method, in situ polymerization, and melt compounding.

Solvent method

This method is based on using a solvent. In this process, the polymer used is soluble, and nanometric additives should be easily dispersed, in which the nanometric additives are treated by their surface modification method. The polymer and nanometric additives are added to water and an organic solvent, and they are mechanically mixed by stirring or ultrasonification. The final step of the preparation method is that the solvent is totally removed from composite by using an oven or vacuum situation oven to precipitate vaporization. The solvents that are mainly used are xylene, toluene, benzene, ethylene acetate, benzene and other organic solvents and can be used to dilute an olefin polymer. Sometimes, water can be used to dilute water soluble polymers, for example, polyethylene glycol (PEG), polyvinyl alcohol (PVA), and polyethylene oxide (PEO). The solvent method is easy to adapt to many cases of polymer nanocomposites because of the materials' solubilities. Nevertheless, as a strong point, it is not too easy to adopt on an industrial scale, as this method needs a lot of time to process, a large amount of solvent, and finally a lot of energy to evaporate the solvent; therefore, it affects the environment and is economically prohibitive [6, 11, 49].

In situ polymerization

In situ polymerization is a very effective method for nanomaterial dispersion. Well-known research involving a polymer/nanoclay composite on PA6 by using in situ polymerization was performed by the Toyota research group [50]. After two decades, much research has been attempted. Normally, the in situ polymerization follows two steps: In the first step, the nanometric particles are added to the monomer, and then they are stirred or sonicated for dispersity. In the second step, the nanomaterial-dispersed monomer solution is polymerized using a normal polymerization method [51]. Particularly, in situ polymerization shows a good dispersity for nanosilicate materials in a Nylon6 matrix [52]. The previous section mentions the importance of the nanoclay's degree of intercalation. These methods are very effective and show a good interaction between the clay and the nylon polymer matrix. After the monomer stat organic monomer is inserted between the clay layers, then the clay layers unfold during the polymerization [53]. However, sometimes rings form from monomer situated between the clay layers. The rings close the d-spacing of the clay layers by a ring opening polymerization when they have less interaction with clay surface [54]. Furthermore, CNT can also be used for in situ polymerization, with solving CNT bundles and dispersion being important factors [55]. Thus, in situ polymerization has strong points regarding nanodispersion with many kinds of polymer and nanometric additives; however, this process has some drawbacks on the industrial scale. First, the materials need a long curing time of over 24 h. Second, sometimes the nanometric additives re-aggregate during the subsequent processing step; therefore, they are not always thermodynamically stable. Finally, this process is suitable to a resin manufacturer who adopts the process on the production line [56].

Melt compounding

Melt blending is a well-known and widely used nanometric additive and polymer compounding process. Melted polymer resin is mixed with nanometric particles in a twin extruder or internal mixer, with forced shear stress and thermodynamic kinetics. Compared with the previous two methods, melt compounding has the advantages that it needs little time and is more economical when adopted to an industrial production line, and the formulation can be easily changed. This

process does not need organic solvent, because the process is more ecofriendly compared with the previous two methods. Melt compounding is largely divided into two groups, dynamic compounding and static compounding. Typically, static compounding uses an internal mixer, and dynamic compounding uses a twin extruder. For convenience and efficiency, the dynamic compounding method is widely used in industry and laboratories. During the melt compounding process, nanometric materials and polymer resin are subjected to shear forces; thus, a nanometric bundle is resolved, and they mix together. However, just using melt compounding falls short in achieving a high dispersity and good clay intercalation because the interaction between the matrix and the novel nanometric particles is weaker than that between the particles. To overcome these drawbacks, a coupling agent can be used, usually a malic anhydride grafted polymer [57, 58]. Otherwise, surface modified nanometric particles or both can be used for good dispersity in a polymer matrix [6, 11, 19, 59].

In this part, we introduced the basic three preparation methods. Each method has pros and cons. For using polymer and nanometric particles, the compounding method should be selected for the best performance based on the dispersity of nanomaterials.

Thermal stability

The concepts of thermal stability and flame retardancy look so similar, but something is different. Both concepts are based on thermal degradation but measure different properties and atmospheres. The thermal stability of polymer-based composite materials is measured by a thermogravimetric analyzer (TGA). TGA can be controlled by an atmosphere furnace, and the technique normally measures thermal stability be using a nitrogen atmosphere condition. On the other hand, when measuring the flame retardancy one uses a novel atmosphere condition. Therefore, thermal stability did not affect the O_2 shielding effect and can be dedicated to the chemical degradation reaction based on thermodynamics.

Despite the general improvement in flame retardancy, decreases in the polymer thermal stability in nanocomposites have been reported, and many diverse mechanisms have been suggested to solve the phenomenon. In this research field, it has been argued that to explain this phenomenon, for example, nanometric additives can accumulate heat during the early stage of exposure to the heat source, and as a result, the nanometric particles accelerate the decomposition of the composite material. This result is connected with the heat flow from the heat source to the polymer composite [60]. Additionally, in the case of an organically modified clay composite, surface modified by organic surfactant, containing alkyl ammonium cations, could be affected by decomposition followed by Hofmann elimination [61]. Furthermore, for an organic surfactant containing a single carbon chain for the tail, the thermal decomposition temperature starts at approximately 180°C [62].



TGA curves for pure ABS and ABS with various PDSPB contents at a heating rate of 10 $^{\circ}$ C /min in N2. [65] With permission. Copyright 2007, Elsevier Ltd.

Exceptionally, intumescent agent/polymer composites, including polymeric synthesized intumescent agents or conjugated with a nanometric surface, show decreasing thermal stability in the intumescent polymer composite. Haiyun*et al.* [65] describe a novel phosphorous-nitrogen structure containing an intumescent flame retardant, poly(4,4-diaminodiphenyl methane spirocyclicpentaerythritol bisphosphonate) (PDSPB), synthesized and compounded with acrylonitrile-butadiene-styrene copolymer (ABS) and characterized it. The thermal stability was measured by TGA in a N2 atmosphere, and Figure 1.10 shows the TGA thermograms of pure ABS and ABS with various PDSPB contents. The TGA results show that the addition of PDSPB reduces the initial degradation temperature, nevertheless incised residue (may as char form) weigh, and it can affect the flammability but not the stability. Comparing PDSPB intumescent agent and ABS copolymer, at degradation starting temperature shows a large gap, even if the polymerized intumescent agent did not overcome the low decomposition temperature.

However, many reports show the increasing of thermal stability of clay nanocomposites because nanoclay acts as an insulator and a thermal barrier to interrupt the diffusion of volatile thermal degradation intermediate materials, as well as supports the char forming process during thermal consumption [6, 63, 64, 66].

As a practical example, Jinet al. [67] studied the fire properties of polystyrene-clay nanocomposites, also using the TGA measured thermal stability of the composite, and they show a dramatic increase compared with the virgin PS, as shown in Figure 1.11, where the degradation temperature is 50 °C higher. The phosphonium nanocomposite, one can see that there is a second step in the degradation, which is absent in the other two materials. This second step accounts for approximately 30% of the degradation of the phosphonium polystyrene nanocomposite and must be attributed to some interaction between the clay and the polymer that serves to stabilize the nanocomposite. The most likely explanation is that the higher decomposition temperature of the phosphonium clay provides the formation of char at a more opportune time to retain the polymer. In the case of the ammonium clays, char formation occurs earlier and can be broken up by the time that the polymer degrades [67].



TGA curves for polystyrene, PS, and the nanocomposites. [67] Reproduced with permission. Copyright 2001, American Chemical Society.

Graphene has a similar morphology to nanoclay and shows similar results regarding thermal stability, when used for nanometrics in a polymer matrix, and many papers show an increased thermal stability of the graphene polymer composite [68]. Nevertheless, graphene should be exfoliated to show a sufficient thermal property. When compared with exfoliated graphite (EG) and natural graphite (NG) in a polylactide matrix as nanometric additive, the thermal stability shows a difference in the TGA curve, as shown in Figure 1.12. In the case of the untreated graphene (natural graphene polymer composite, the TGA curve is undistinguishable. Furthermore, 0.5 wt% of NG composite TGA curve is lower than that of the neat PLA resin. Only the residue of the composite at temperatures over 400°C amount wt% was increased proportionally with the initial NG feed content in the composite. EG and NG composites were compared regarding their thermal stabilities, thermal degradation temperature at 5%, and 50% weight losses point (T5% and T50%), evaluated by the TGA method. T5% and T50% of polylactidehomopolymer were determined to be 350°C and 386°C, respectively. For instance, the T5% of the PLA/EG nanocomposite with 3.0 wt % EG was ~364°C, which is ~14 K higher than that of PLA homopolymer. This improved thermal stability of PLA/EG nanocomposites is believed to originate from the fact that graphite nanoplatelets of EG, which were dispersed homogeneously in the PLA matrix, serve as the mass transfer barriers against the volatile pyrolized products in the PLA matrix, eventually retarding thermal degradation of the nanocomposites [69].



TGA curves of (A) PLA/EG and (B) PLA/NG composites with various graphite contents. [69] With permission. Copyright 2010, Wiley Periodicals, Inc.

In this flame retardancy part, carbon nanotubes are finally described. CNT morphology is different with layered silicate and graphene; they have a two dimensional morphology. Thus, they have a different property and form a different carbonization structure, when they are used as a nanometric additive in a polymer matrix. They form a fibrous three dimensional network structure, which has an effect on the composite when exposed heat sources and thermal degradation processes, with improved thermal stability of CNT polymer composites in those conditions [70]. In contrast, CNT polymer composites show different TGA curb behavior; as CNT contents increase, thermal stability is decreased. They decreased the thermal stability of the composites in nitrogen condition. This is probably due to the remnant catalyst in the SWNT hastening the decomposition, and also the decomposition starting as the temperature was diminished [71].

Widely used organic flame retardants have low thermal stability and degradation starting temperatures. For these reasons, organo-containing flame retardant composites and nanocomposites show low decomposition starting temperatures [1-3, 18, 20]. To overcome these drawbacks, nanometric additives are used together when making polymer composites. Alternatively, intumescent agents reacted on nanometric or polymerized together [18, 24, 29-30, 39, 43].

As seen before, thermal stability was decreased, following an increase in the mass ratio of nanometric or intumescent agents in polymer composites, as evaluated by using TGA under nitrogen condition. These results are based on chemical degradation; nanometric materials affect flammability by forming a three-dimensional network structure, and this structure interrupts intermediate diffusion of intermediate materials to meet oxygen in the air at the consuming reaction surface. However, using TGA under nitrogen condition, these effects are insignificant to rising thermal stability.

Flame Retardancy

In this chapter, flame retardancy already mention about impotency of. Many methods exist to

evaluate flame retardancy, but among the many methods, the cone calorimeter has been the one mainly and widely used by researchers. The cone calorimeter provides many kinds of valuable information and indicates the flame retardancy. Mainly, these tests follow standard methods, such as ASTM 1354 and ISO 5660, and they provide the oxygen consumption rate. Obtained indications of oxygen change value are calculated to amount of heat energy during polymer consumption. The cone calorimeter experiment uses radiant heat to irradiate the sample, mainly at 35 or 50 kW/m2. The experiment provides information on many properties, including heat release rate (HRR), peak of heat release (PHRR), time to ignition (TTI), total heat released (THR), and mass loss rate (MLR). The HRR and MHRR are mainly used as the most valuable indicators of flame retardancy [72, 73].

In many research papers have described enhanced flame retardancy using nanometric additives and intumescent agents, when compared with novel polymer [4-11, 15, 20-32]. Thermal stability and Flame retardancy properties look similar but are different, considering the degradation mechanism and experiment condition. When comparing the two properties from the viewpoint of degradation mechanism, thermal stability was degraded under oxygen restricted conditions; thus, they were just affected by thermal energy, and there was no interference by oxygen. However, flame retardancy occurs under novel air conditions; therefore, it is naturally affected by oxygen, and during the process, samples are affected by the structure formed by nanometric additives or intumescent agents. These three dimensional network structures hinder the degraded intermediate materials from moving to meet with oxygen and shield the heat energy formed by the heat source. For these reasons, some nanocomposite polymer and intumescent polymer composite show low thermal stability, but on the contrary, they show good flame retardancy. Flame retardancy is such a complicated property because it is affected by chemical structure and additive dispersity of residuals forming and by the reciprocal action between composite elements of organic and inorganic materials under air conditions.

Zanetti and Costa [74] studied the nanosilicate polymer composite consumption process; when using an EVA-based nanocomposite that showed enhanced flammability, HRR and MLR were reduced 70-80% with silicate lodging 2-5%. These results are due to the formation of clay-char; these structures have refractory properties and porous structures. During the consumption process, clay-char layer formed by the silicate clay reassembles during charring process of the polymer.

Kashiwagi*et al.* [75] studied the flammability of a CNT polymer nanocomposite material and a carbon black (CB) polymer composite. CNTs have a different morphology compared with nanosilicate or graphene; silicate or silicate clay have a two-dimensional plate type morphology, while CNTs have one-dimensional wire like morphology. However, CNT composites have similar mechanisms, CNT also produce residual form, have CNT structural core. As shown at Figure 1.13 CNT polymer nanocomposite show low HRR graph compare with a novel polypropylene resin. 1% CNT/PP composite shows the lowest heat release rete; the reason for the lowest PHRR is due to the balance between the effect of thermal conductivity and the shielding performance of external radiant flux (and heat feedback from the flame) depending on the concentration of MWNT in the sample. A nanotube network layer consisting of carbon nanotubes is formed, and it covers the entire sample surface without any significant cracks forming during burning.



TGA (a) Effects of concentration of MWNT in PP on heat release rate of PP/MWNT nanocomposite at 50 kW/m^2 . (b) SEM picture of MWNT dispersion in the PP/MWNT(4%) nanocomposite after solvent removal of PP. (c) Collected residues after the gasification experiment at 50 kW/m^2 in nitrogen about PP/MWNT(1%). [75] Reproduced with permission. Copyright 2004, Elsevier Ltd.

Graphene has a chemical structure similar to CNTs, composed of sp₂ carbon atoms arranged in a honeycomb structure, and the same morphology as nanosilicate clay's two-dimensional sheet. When MMT, CNT, and graphene are compared with the same 3 wt% of nanometric polymer composite for flammability using a cone calorimeter, they have different behaviors, as shown in Figure 1.14. Compared to pure PVA, the PHRR of PVA-G3 is reduced by 49% and is lower than those of PVA-MMT and PVA-MWNTs. To explain this unexpected fire behavior, morphologies of the final chars after cone calorimeter tests of the PVA composites were based on graphene nano-sheets by using SEM. The SEM images (Figure 1.14 b) for the residues of PVA-G3 after cone calorimeter tests showed that many quadrate carbonaceous particles $(1-3 \ \mu m)$ joined each other and formed the compact, dense and uniform char. The graphene can promote the formation of compact char layers in condensed phase during combustion of the polymer matrix. Furthermore, the char structure effectively prevents the inside thermal decomposition products into the flame zone and that of the O2 into the underlying polymer matrix [26].



(a) Cone calorimeter experiments, heat release rate versus time curves: comparison of the effect of the 3wt% different nanofillers (Na-MMT, MWNTs and graphene). (b) Morphologies of the final chars after cone calorimeter tests of PVA-Graphene 3wt% composite. [26] Reproduced with permission. Copyright 2011, Elsevier Ltd.

These nanometric composites showed good flammability compared with novel polymer resin. In addition, they can have synergetic effect on flammability, when they are used together in a polymer matrix as additives. Sepiolitenanoclay (Sep) has a unique morphology in the class of nanoclay, and CNT creates a network, forming a tight char. Clay and CNT both create char layers. When they are used together, the clay and CNT hybrid composite makes a much higher density network form, when compared with other CNT/PP or clay/PP composite cone calorimeter residue, shown in Figure 1.15. Thus, the PHRR can be dynamically decreased from a novel PP of 1,933 kW/m² to PP/CNT/Sep composite of 355 kW/m² for the 10wt% Sepiolite + 2wt% MWNT ternary nanocomposites system, these result originated from a higher density char residue. The use of sepiolitenanoclay in combination with multi-walled CNTs showed that the PHRR was significantly reduced by 82% compared to the neat polymer in the cone calorimeter shown in Figure 1.15 [76]. Marosfoil*et al.* also studied the flame retardancy performance of CNT filled PP and managed to reduce the PHRR from 2,755 kW/m² to 760kW/m² for PP and PP/CNT, respectively [76, 77]. In this way, using different morphological nanometric additives can lead to synergetic flammability performance.

The non-halogen Intumescent agent system was widely studied and is now used for additive in flame retardant composite materials [1, 34, 35, 65]. These flame retardants consist of three basic elements, mainly ammonium polyphosphate (APP)/ pentaerythritol (PER)/ melamine (MER). However, the flame retardant mechanism of APP/PER has been investigated, but it is very complicated; the study of flame retardant mechanism between APP and oligomeric char forming agents was established. Furthermore, the traditional IFR additives are susceptible to migration onto the polymer surface during processing, owing to their low molecular weight, and thus decreasing the flame retardant efficiency. To solve these shortcomings, high molecular weight, namely oligomeric or polymeric IFRs, have been developed, which provides a good strategy to solve the above problems [78]. These polymerized intumescent agent containing polymer composites show good flammability. Peng *et al.* [42] studied these kinds of intumescent agent systems BCPPO and achieved a low PHRR value for 122.7 kW/m² compare with novel PP resin for 729.6 kW/m²; they were successfully exerted in the intumescent system.



(a) Heat release rate versus time chart for unfilled PP and ternary PP nanocomposite (10 wt.% Sep + 2 wt.% MWNT). SEM images of (b) PP + CNT (c) PP + Sep and (d) PP ternary system post cone calorimeter test. [76] Reproduced with permission. Copyright 2012, John Wiley & Sons, Ltd.

Both nanometric additives and intumescent agents can accomplish good flammability, and when they are used for additives in polymer composites, they show synergetic flammability performance. PDSPB intumescent agent and MMT clay were used for additives of ABS based polymer composites, and they were compared with clay composite and MMT composite. During composite blending process MMT clay be exfoliated affect by PDSPB, so the ABS/PDSPB/MMT composite has high dispersity and Specific surface area compared with the ABS/MMT composite, as shown at Figure 1.16 (c, d). These clay-intumescent hybrid composites show blameless efficiency, compared with other composites' achievement of flammability. The ABS/PDSPB/MMT composite is made of PDSPB 18wt% and MMT 2wt%; nevertheless, it shows a flammability value lower than the ABS/PDSPB 30wt% composite sample, as shown at Figure 1.15(a). How do these composites show synergetic performance? The acid source in PDSPB of phosphoric acid is deformed as an acid catalyst by heat energy. They related the dehydration process to making carbonific compound. The phosphoric acid has close association about forming silicoaluminophosphate (SAPO); these processes are illustrated in Figure 1.16 (b) [79].



(a) Heat release rate (HRR) of ABS, ABS/montmorillonite 2wt%, ABS/PDSPB 20 and 30wt% blends and ABS/PDSPB/MMT, 80/18/2wt% at 35 kW/m2. (b) The proposed structure of SAPO and final chars for ABS/PDSPB/MMT. (c) TEM micrographs ABS/montmorillonite (d) TEM micrographs ABS/PDSPB/MMT. Reproduced with permission. [79] Reproduced with permission. Copyright 2007, Elsevier Ltd.

In the same vein, hybrid formulation about organic intumescent system and other nanometric additives, such as CNT and graphene, is expected to have a synergetic flammability effect. Ma *et al.* [24] grafted PDSPB on MWNT, obtaining MWNT-PDSPB as shown in Figure 1.5. MWNT-PDSPB also achieved good dispersity in the composite and improved flammability. Graphene also has been grafted polymerized in various organic-inorganic intumescent systems, and the adapted polymer composite has high thermal stability and flammability [29, 30].

Conclusion

In this chapter, we investigate about flammability of nanometric polymer composite and intumescent system. The representative nanometric materials, including nanoclay, carbon nanotube and graphene, referred to in this chapter can be used as flame retardancy additives. In addition, an organic intumescent system was summarized regarding its chemical composition and mechanism. Occasionally nanometric additives, for achieving high flammability, have priority for dispersity in polymer composites. In the case of clay, it should be modified on the surface to make clay intercalate and an exfoliated state. To solve these problems, the nanometric additives surface is grafted by polymer consisting of an intumescent agent system element. Composites that contain

intumescent agents grafted nanometric additives show advanced flame retardancy. Using different kinds of nanometric additive together in the composite resulted in synergetic flame retardancy originating from the morphological properties. Additionally, reactions between the intumescent agent and the nanosilicate surface result in the formation of carbonic char, and this reaction is the reason for the synergetic effect on flammability. Finally summarizing this chapter, flammability has many complicated reasons, including chemical properties and physical properties originating from morphology, and when additives are used together, they can have synergetic outcomes.

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